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INK JET RECORDING SHEET AND ITS MANUFACTURE

[Claim(s)]

[Claim 1]An ink jet recording sheet having a starch particle layer which uses an aquosity binder as the main ingredients with a starch granule child between this base material and an ink receiving layer in an ink jet recording sheet which has the above ink receiving layer further at least on one side of a base material.

[Claim 2]A manufacturing method of an ink jet recording sheet painting an ink receiving layer on a base material which has a starch particle layer which uses an aquosity binder as the main ingredients with a starch granule child in an ink jet recording sheet which has the above ink receiving layer further at least on one side of a base material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the ink jet recording sheet which records using a water-based ink. In detail, record density is high, the strike-through of the nonuniformity of a recording part, BOKOTSUKI, and ink is decreased remarkably, and it is related with the ink jet recording sheet excellent in the conveyance nature in a printer, and its manufacturing method.

[0002]

[Description of the Prior Art] An ink jet recording method makes the minute drop of ink fly by various working principles, is made to adhere to record sheets, such as paper, and records a picture, a character, etc.

There is which feature that does not need development-fixing with the large flexibility of ease [a high speed, a low noise, and multiple-color-izing] and a recording pattern, and it has spread through various uses quickly as recorders, such as various figures and a color picture, including a Chinese character.

[0003] Various efforts have been made from a device or the field of an ink presentation so that the paper of fine quality and coated paper which are used for usual printing and note can be used as a record sheet used with this ink jet recording method. However, it came to be required with improvement in the performance of ink-jet recording devices, such as improvement in the speed of a device, highly-minute-izing, or full-color-izing, or expansion of a use that it should have the following advanced characteristics also to a record sheet.

- (1) Usually, excel in the conveyance nature at the time of recording with a recorder.
- (2) The strike-through of the picture recorded on the surface and a cockring should be prevented, and a high-definition recorded image should be obtained under wide range temperature-and-humidity conditions.
- (3) Record dot concentration and image concentration are high.
- (4) Picture color nature and clear nature are good.
- (5) Print dot shape is good.
- (6) Ink absorbency is good.
- (7) Image keeping quality, such as the water resisting property of a recorded image, lightfastness, and ozone resistance, is good.

(8) At a coat type record sheet, the adhesive property of a coating layer is high and there is little powder omission.

(9) Yellowing of the record sheet itself should not take place easily.

(10) as compared with the dot diameter in a monochrome part, the dot diameter in a color overlapping part hardly changes -- a color overlapping part -- ooze out, and there is no ***** and a high definition recorded image should be obtained.

[0004]Paying attention to the improvement of specific performance, much proposals are made former among these. For example, to JP,62-282967,A. In order to improve ink absorbency, the optical density of a recorded image, glossiness, curl-proof nature, etc., it has an ink holding layer and an ink transporting bed on a substrate, and also the same as that of an ink holding layer or the recorded material provided with the curl restraining layer which has similar physical properties is indicated. In order to improve ink absorbency, picture clear nature, conveyance nature, etc., the example which provided the curl prevention layer which becomes the recorded material provided with the ink absorbing layer from resin, such as polyacrylamide, is indicated by JP,61-235184,A. To JP,62-162586,A and JP,62-162587,A. By providing the layer which comprises the granular material of a **** minute amount ($0.01 \sim 1.0 \text{ g/m}^2$) in the opposite side of a recording layer (film base), or the field of both sides, the recorded material which raised the sheet transportation nature and blocking resistance of the printer is indicated.

[0005]

[Problem(s) to be Solved by the Invention]However, although the recorded materials (JP,62-282967,A etc.) provided with the aforementioned curl control and prevention layer improve contact with a printer head by curl control and prevention and aim at improvement in conveyance nature, In the printer which uses especially a cut sheet, it originates in the character of the sheet itself and there is still a problem that continuous recording where is poor, therefore it tended to produce the defect of conveyance nature, such as jamming (paper jam), bias, and a double feed, and was stabilized is not made. [of the pickup in the case of feeding]

[0006]There is a problem that it is not what should also satisfy conveyance nature with powder omission (JP,62-162586,A etc.) in the recorded material provided with the layer which comprises the aforementioned granular material.

[0007]This invention solves these problems and besides the outstanding conveyance nature by the good pickup in the case of feeding, It has high record density required in order to carry out ink jet recording using a water-based ink, and aims at providing an ink jet recording sheet provided with many performances, such as powder omission

performance in which decreased remarkably and the nonuniformity and BOKOTSUKI of the recording part were excelled, and a manufacturing method for the same.

[0008]

[Means for Solving the Problem]In an ink jet recording sheet in which this invention has the above ink receiving layer further at least on one side of a base material in order to attain this purpose, They are an ink jet recording sheet painting an ink receiving layer on a base material which gave a starch particle layer which uses an aquosity binder as the main ingredients with a starch granule child to the surface, and its manufacturing method.

[0009]In an ink jet recording sheet of this invention, a starch granule child given to a support surface, Adhesive strength between base materials is improved with an ink receiving layer, maintaining ink absorbency by forming a layer system, with particle shape maintained, Powder omission from an ink receiving layer is prevented, and the pick up roll at the time of taking up a record sheet one by one from a bunch of a record sheet installed in a printer and a slip between record sheets are prevented.

[0010]Unevenness of a support surface is decreased, color distribution by an ink receiving layer containing a color fixing agent is equalized by equalizing an ink receiving layer's thickness, and density unevenness of the Records Department resulting from localization of a color is canceled. Besides, in addition, BOKOTSUKI of a recording part of a record sheet and a strike-through of ink are prevented by delaying osmosis on paper of a color and a separated ink solvent by the above-mentioned ink receiving layer.

[0011]As a starch granule child used for a starch particle layer of this invention, Following (b) · (**) which processed a thing manufactured from raw materials, such as corn (cornstarch), wheat, barley, rice, a potato (potato), a cassava (tapioca), a sweet potato (sweet potato), and sago, or these can be mentioned, and especially amyllum-oryzae powder is preferred.

(b) Oxidized starch produced by oxidizing with oxidizers, such as sodium hypochlorite.

(**) Acid treatment starch processed with chloride, sulfuric acid, etc.

(**) Enzyme treatment starch.

(**) Dialdehyde starch made to react with periodic acid.

(**) Esterification starch, such as acetylation starch, urea phosphorylation starch, and phosphorylation starch.

(**) Etherification starch, such as hydroxyalkyl-ized starch and carboxy alkylation starch.

(**) Cation-ized starch.

(**) Cross crosslinking starch, such as formaldehyde cross crosslinking starch, epichlorohydrin cross crosslinking starch, and phosphoric acid cross crosslinking starch.

(**) Graft polymerization starch produced by polymerizing in starch which built the active spot with cyclic monomers, such as vinyl monomers, such as acrylic acid, acrylonitrile, acrylamide, methacrylic acid ester, and vinyl acetate, epoxide, episulphide, imine, and lactam.

[0012]in order to maintain particle shape in an ink jet recording sheet of this invention among these starch granule children, what there is no chilled water fusibility or is not almost is preferred, and there is almost no fusibility with water 40 ** or less -- gelatinization -- it is desirable for starting temperature to be not less than 50 **. In order to satisfy adhesive strength with an ink receiving layer, a rate of absorption of ink and an absorbed amount, and grace of a recorded image, it is desirable still more preferred to consider it as the range of 1-20-micrometer volume mean particle diameter, and a range of both starch particle diameter is 2-10 micrometers. As for a starch particle layer of this invention, it is preferred to comprise an above-mentioned starch granule child and a water polymer binder, and a water polymer binder has a preferred five or more weight section 100 weight-section medical department to starch granule child 100 weight section. As for a water polymer binder, less than five weight sections will not be enough as intensity of a starch particle layer, and it will produce a slip between the pick up roll resulting from an ink receiving layer's desorption, and a record sheet in them. If a water polymer binder exceeds 100 weight sections, opening sufficient in a starch particle layer will not be generated, but ink absorbency aggravation will be caused, and recording performance will fall.

[0013]As a water polymer binder used for a starch particle layer of this invention, For example, starch derivatives, such as oxidized starch, etherification starch, and phosphorylation starch; Carboxymethyl cellulose, Cellulosics, such as hydroxyethyl cellulose; Casein, gelatin, Polyvinyl alcohol derivatives, such as soybean protein, polyvinyl alcohol, or silyl denaturation polyvinyl alcohol; A polyvinyl pyrrolidone, Maleic anhydride resin, a styrene butadiene copolymer, conjugated diene system copolymer latex [, such as a methyl methacrylate butadiene copolymer,]; -- acrylic (**) polymer latex [, such as a polymer of acrylic ester and methacrylic acid ester, or a copolymer,]; -- vinyl system copolymer latex [, such as an ethylene-vinyl acetate copolymer,]. Or these functional group denaturation (**) polymer latex according several kinds (**) to functional group content monomers, such as a carboxy group of a polymer; Melamine resin, Water borne adhesive, such as heat-curing synthetic resins, such as urea resin; A polymer of acrylic ester, such as polymethylmethacrylate, and

methacrylic acid ester or copolymer-resin; polyurethane resin, unsaturated polyester resin, a VCM/PVC vinyl acetate copolymer, A polyvinyl butyral and an alkyd resin can be mentioned. Use of starch derivatives, such as oxidized starch from a point of recording performance and adhesive strength, etherification starch, and phosphorylation starch, is preferred among these water soluble binders. In addition to this water polymer binder, a white inorganic pigment, a cationic color fixing agent, a surface-size agent, and other additive agents may contain in a starch particle layer in this invention for the purpose of improvement in recording performance, and ink-absorption-velocity control.

[0014]Below 20 g/m^2 of a coating amount of a starch particle layer is [more than 2 g/m^2] preferred, Moreover a layer is not constituted as it is less than 2 g/m^2 , and sufficient effect is not acquired, if 20 g/m^2 is exceeded, the color enhancement of a color will fall under influence of a starch granule child's concealment nature, and a fall of record density will be produced.

[0015]As for an ink receiving layer of this invention, it is preferred to constitute a white inorganic pigment, a water soluble binder, and a cationic color fixing agent as the main ingredients. As said white inorganic pigment, for example Calcium carbonate, kaolin, talc, Calcium sulfate, barium sulfate, a titanium dioxide, a zinc oxide, zinc sulfide, Zinc carbonate, a satin white, aluminum silicate, diatomite, a calcium silicate, a magnesium silicate, synthetic amorphous silica, quasi-boehmite, aluminium hydroxide, alumina, lithopone, zeolite, hydrated halloysite, magnesium carbonate, magnesium hydroxide, etc. are mentioned. In this, porosity composition amorphous silica with large pore volume is preferred. A starch granule child can also be used.

[0016]The 1st class - the tertiary amine or a monomer of quaternary ammonium salt, oligomer, and polymer which dissociate as a cationic color fixing agent when it dissolves in water, and present cationicity can be mentioned, and they are oligomer or polymer preferably. A cation loading dose according to the colloid titration method especially is a cationic color fixing agent of $1 \sim 10 \text{ meq./g}$. By less than 1 meq./g , fixing performance of water soluble dye in a water-based ink is inferior, and the water resisting property of a recorded image falls. When 10 meq./g is exceeded, the water resisting property of a recorded image can be improved in a small quantity, but lightfastness and ozone resistance of a recorded image are inferior, and the xanthochroism of a record sheet gets worse.

[0017]Said white inorganic pigment in a starch particle layer of an ink jet recording sheet of this invention and an ink receiving layer, a starch granule child, a water polymer binder, and cationic color fixing agents may be one sort or two sorts or more of

mixtures, respectively.

[0018]In an ink receiving layer in this invention, said water polymer binder receives white inorganic pigment 100 weight section, a water polymer binder -- ten to 100 weight section, and a cationic color fixing agent -- as 0.1 - 5 g/m² and a cation loading dose -- 0.1 - 50 meq/m² ** rare ***** -- things are preferred.

[0019]As a base material in this invention, paper or a thermoplastic resin film, a synthetic paper, a synthetic resin laminated paper like a base material for photographs, and a sheet-shaped substance like a nonwoven fabric which made wood fibers and a synthetic fiber a subject are mentioned. In the case of paper, sizing compounds, such as addition of an internal sizing compound, additive-free, a neutral size agent, a polymer sizing compound, and an acid sizing compound, are independent, or any of concomitant use use, content of a loading material, or not containing may be sufficient, and there is no restriction in any way. As a white pigment, conventionally, publicly known paints are independent, or use together internal loading material of a base paper, and it is used.

[0020]As a preparation method of an ink jet recording sheet of this invention, Disaggregate a pulp fiber, consider it as a slurry, and if needed For example, a loading material and a sizing compound, Other additive agents are added, and it mills paper and dries with a paper machine, or coating of the water soluble polymer binder is carried out to a starch granule child by size press or gate roll coater after paper milling, it dries, and a machine calendar is covered. Or after obtaining a substrate sheet, a starch particle layer is provided using a coating apparatus or a size press device. As a method of providing an ink receiving layer, any of an one machine coating machine and an off-machine coating machine may be sufficient. Calendering is further performed after coating. An ink receiving layer's coating amount has the preferred range of 5 - 30 g/m².

[0021]To a base material in an ink jet recording sheet, a starch particle layer, and an ink receiving layer of this invention. As other additive agents, **** combination of the colloidal silica, pigment agent, thickener, fluidity improving agent, defoaming agent, foam suppressor, release agent, foaming agent, penetrating agent, ** motorcycle agent, water resistance-ized agent, humid paper reinforcing agent, and dry paper reinforcing agent etc. can also be carried out.

[0022]Water-based inks as used in the field of this invention are colorant, a solvent, and a recording ink object that consists of other additive agents. As colorant, water soluble dye, such as a direct color, acid dye, a basic stain, reactive dye, or a food dye, is mentioned. As a solvent of a water-based ink, water and water-soluble, various organic solvents are mentioned. As other additive agents, a pH regulator, a sequestering agent,

an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surface-active agent, and a rust-proofer are mentioned, for example.

[0023]

[Example] Although the example of this invention is given and described below, this invention is not limited to these examples. Especially a "part" and "%" shown in an example, unless it shows clearly, weight section and weight % is shown.

[0024] To the pulp slurry which comprises 67 copies of LBKP(s) of comparative example 1 freshness 450mlCSF, and eight copies of NBKP(s) of freshness 450mlCSF. 0.6 copy of cation starch, ten copies of talc, ten copies of heavy calcium carbonate, five copies of precipitated calcium carbonate, and 0.1 copy of alkyl ketene dimer are added, pH of pulp slurry was adjusted to 8.2, paper-milling desiccation was carried out with the Fourdrinier machine, it impregnated and dried so that it might become double-sided 5 g/m² by solid content about 10% of concentration oxidized starch solution by size press continuously, and machine calendering was carried out further, and the coating stencil paper of basis weight 63 g/m² was obtained. On this coating stencil paper, 75 copies of synthetic amorphous silica (the fine seal X37B, the Tokuyama Soda Co., Ltd. make), 25 copies of synthetic amorphous silica (Syloid 620, product made by Fuji DEVISON), 20 copies of polyvinyl alcohol (PVA117, Kuraray Co., Ltd. make), and a cationic color fixing agent (the SUMIRETTSU resin 1001 and the Sumitomo Chemical Co., Ltd. make.) Coating of the coating liquid of 18% of the concentration which blended the cation loading dose 3.5meq./g30 copy was carried out so that it might become solid content 10 g/m² by an air knife coater, and the maximum temperature of the hot wind was dried as not less than 120 **.

[0025] To the pulp slurry which comprises 67 copies of LBKP(s) of example 1 freshness 450mlCSF, and eight copies of NBKP(s) of freshness 450mlCSF. 0.6 copy of cation starch, ten copies of talc, ten copies of heavy calcium carbonate, five copies of precipitated calcium carbonate, and 0.1 copy of alkyl ketene dimer are added, Adjust pH of pulp slurry to 8.2 and paper-milling desiccation is carried out with a Fourdrinier machine, The impregnating liquid of 10% of the concentration which blended ten copies of oxidized starch with 100 copies of amylum-oryzae particles (mean particle diameter of 4 micrometers) as an aqueosity binder by size press continuously, It impregnated and dried so that it might become double-sided 4.5 g/m² by solid content, and the ink jet recording sheet of Example 1 was obtained like the comparative example 1 except having carried out machine calendering further and having obtained the coating stencil paper of basis weight 63 g/m².

[0026] By the comparative example 2 comparative example 1, instead of carrying out the

size press of the oxidized starch solution, Coating of the oxidized starch solution of 20% of concentration was carried out by gate roll coater so that it might become 3.2g/m double-sided ² by solid content, and the ink jet recording sheet of the comparative example 2 was obtained like the comparative example 1 except having obtained the coating stencil paper of basis weight 63 g/m².

[0027]By the example 2 comparative example 1, to the pulp slurry which comprises 60 copies of LBKP(s) of freshness 380mlCSF, and 15 copies of NBKP(s) of freshness 480mlCSF. 0.6 copy of cation starch, 20 copies of heavy calcium carbonate, 15 copies of precipitated calcium carbonate, and 0.1 copy of alkyl ketene dimer are added, Adjust pH of pulp slurry to 8.2 and paper-milling desiccation is carried out with a Fourdrinier machine, The coating liquid of 40% of the concentration which blended 20 copies of oxidized starch with 100 copies of amylum-tritici particles (mean particle diameter of 12 micrometers) as an aquosity binder continuously by gate roll coater so that it may become double-sided 6 g/m² by solid content Coating, It dried and the ink jet recording sheet of Example 2 was obtained like the comparative example 1 except having carried out machine calendering further and having obtained the coating stencil paper of basis weight 87 g/m².

[0028]By the example 3 comparative example 1, to the pulp slurry which comprises 60 copies of LBKP(s) of freshness 380mlCSF, and 15 copies of NBKP(s) of freshness 480mlCSF. 0.6 copy of cation starch, 20 copies of heavy calcium carbonate, 15 copies of precipitated calcium carbonate, and 0.1 copy of alkyl ketene dimer were added, pH of pulp slurry was adjusted to 8.2, paper-milling desiccation was carried out with the Fourdrinier machine, machine calendering was carried out, and the stencil paper of basis weight ² of 75g/m was obtained. Coating of the coating liquid of 40% of the concentration which blended five copies of polyvinyl alcohol (PVA117, Kuraray Co., Ltd. make) on one side of this stencil paper as 100 copies of amylum-oryzae particles (mean particle diameter of 4 micrometers) and an aquosity binder is carried out by an air knife coating machine so that it may become 12 g/m² by solid content, The ink jet recording sheet of Example 3 was obtained like the comparative example 1 except having obtained basis weight 87 g/m² coating stencil paper.

[0029]In example 4 Example 3, 50 copies of amylum-oryzae particles (mean particle diameter of 4 micrometers), Coating of the coating liquid of 22% of the concentration which blended 20 copies of polyvinyl alcohol (PVA117, Kuraray Co., Ltd. make) with synthetic amorphous silica (Syloid 620, product made by Fuji DEVISON) as an aquosity binder is carried out by an air knife coating machine so that it may become 12 g/m² by solid content, The ink jet recording sheet of Example 4 was obtained like the

comparative example 1 except having obtained basis weight 87 g/m² coating stencil paper.

[0030]In comparative example 3 Example 3. Coating of the coating liquid of 17% of the concentration which blended 20 copies of polyvinyl alcohol (PVA117, Kuraray Co., Ltd. make) with 100 copies of synthetic amorphous silica (Syloid 620, product made by Fuji DEVISON) as an aqueosity binder is carried out by an air knife coating machine so that it may become 12 g/m² by solid content, The ink jet recording sheet of the comparative example 3 was obtained like the comparative example 1 except having obtained basis weight 87 g/m² coating stencil paper.

[0031]By the example 5 comparative example 1, instead of carrying out the size press of the oxidized starch solution, Coating of the coating liquid of 20% of the concentration which blended 100 copies of oxidized starch with 100 copies of amyllum-oryzae particles (mean particle diameter of 4 micrometers) as an aqueosity binder is carried out by gate roll coater so that it may become double-sided 5.0 g/m² by solid content, The ink jet recording sheet of Example 5 was obtained like the comparative example 1 except having obtained the coating stencil paper of basis weight 64 g/m².

[0032]<Performance> Measurement of the performance of an ink jet recording sheet was performed by the following method.

(1) printing record density printing density using an ink jet printer (BJC-820J, Canon, Inc. make) -- a black seal impression -- the character part was measured using the Macbeth RD-918 type.

(2) The nonuniformity of the nonuniformity Records Department of the Records Department used the ink jet printer (MJ-700V2C), performed cyanogen solid printing by the super fine mode, and carried out visual evaluation of the density unevenness of the Records Department.

Valuation-basis O: The Records Department is not permitted density unevenness.

** : The Records Department is permitted density unevenness very slightly.

x : Density unevenness is conspicuous to the Records Department.

(3) BOKOTSUKI of the Records Department and BOKOTSUKI of the strike-through Records Department of ink carried out blue (cyanogen + magenta) solid printing using the ink jet printer (BJC-600J, Canon, Inc. make), and carried out visual evaluation of the BOKOTSUKI state of the Records Department after neglect desiccation one whole day and night. Visual evaluation of the strike-through of ink was carried out collectively. BOKOTSUKI valuation-basis O: The Records Department is not permitted BOKOTSUKI.

** : The Records Department is permitted BOKOTSUKI slightly.

x: The Records Department is permitted BOKOTSUKI clearly.

Strike-through valuation-basis O: An ink strike-through is not observed in the Records Department rear face.

** : The Records Department is permitted an ink strike-through slightly.

x: The Records Department is permitted an ink strike-through.

(4) Conveyance nature conveyance nature carries out attachment ***** of the cut-sheet feeder at an ink jet printer (BJ-10V, Canon, Inc. make), and under the environment of 20 ** and 65%RH, After holding the end of the ink jet recording sheet and generating poor feeding compulsorily, the number of sheets of the accident sheet at the time of letting 100 sheets pass estimated.

The accident number of sheets per A:100 valuation bases is 0-1 sheet.

The accident number of sheets per B:100 sheets is 2-10 sheets.

C: Poor feeding generating was carried out and 100 sheets were not able to be conveyed.

[0033]The measurement result of the performance of the ink jet recording sheet of the comparative examples 1-2 and Examples 1-3 is shown in the following table 1.

[0034]

[Table 1]

	比較例			実施例				
	1	2	3	1	2	3	4	5
記録濃度 (黒)	1.35	1.38	1.40	1.39	1.42	1.38	1.38	1.44
記録部濃度ムラ	×	×	○	○	○	○	○	△
記録部ボツキ	×	△	△	○	○	○	○	○
インク裏抜け	×	△	△	○	○	○	○	○
搬送性	C	C	C	B	B	A	B	A

[0035]

[Effect of the Invention]The ink jet recording sheet of this invention is having a starch particle layer which uses an aquosity binder as the main ingredients with a starch granule child between a base material and an ink receiving layer, The strike-through of the nonuniformity of the recording part at the time of carrying out ink jet recording using a water-based ink, BOKOTSUKI, and ink decreased remarkably, and also the problem by the slip of the pick up roll in the case of feeding resulting from the powder omission from a sheet that a pickup was poor was solved, and the stable continuous printing became possible. That is, it has high record density required in order to carry out ink jet recording using a water-based ink by this invention, There are few strike-throughs of the nonuniformity of a recording part, BOKOTSUKI, and ink remarkably, and an ink jet recording sheet with the outstanding conveyance nature by

good pickup performance and its manufacturing method are provided.

Abstract:

PURPOSE: To provide an ink jet recording sheet and its manufacturing method wherein water-color ink is used, recording density is high in ink jet recording, and it is equipped with an excellent carrying property as well as characteristics wherein an irregularity in a recorded part, its depressed state, and strike through of ink are little.

CONSTITUTION: At least one ink accepting layer is provided on one side of a base material, and a starch grain layer is provided between the base material and the ink accepting layer. The ink jet recording sheet is manufactured by coating the ink accepting layer on the base material having the starch grain layer wherein starch grain and an aqueous binder are main constituents.